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Thermodynamics of lanthanide quinolinate complexation in aqueous solution

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Abstract

The thermodynamic parameters (ΔG_{101}, ΔH_{101} and ΔS_{101}) of formation of 1 : 1 complexes between lanthanide cations and quinolinate have been measured using potentiometric and calorimetric techniques in aqueous solution of 0.50 M ($NaClO_4$) ionic strength at 25 ° C. The thermodynamic data are discussed and are found to indicate a structure in which the quinolinate ligand is coordinated to the lanthanide cation by forming a chelate through the ring nitrogen atom at position 1 and the carboxylate group at position 2 of the pyridine ring.

INTRODUCTION

Thermodynamic studies on the complexation of trivalent lanthanide cations with various heterocyclic carboxylate ligands have been reported [1–9]. The exothermicity of the complexation and the relatively large stability constant of the lanthanide complexes of α-picolinate suggest that the ring nitrogen coordinates to the metal ion together with the α-carboxylate group of the ligand [3–5]. However, the thermodynamic parameters of the furoate complexation indicate that the ring oxygen is not involved in the formation of a chelate ring [9]. In the case of dipicolinate complexes of lanthanide cations, the ring nitrogen as well as two carboxylate groups at positions 2 and 6 of the pyridine ring coordinate to the metal ion to form a double chelate ring [1,2]. As a result the complexes are unusually stable.

We have reported the stability constants and the thermodynamic parameters of the lanthanide pyrazinecarboxylates in aqueous solution [7,8]. Again it was found that the 1-nitrogen atom and the 2-carboxylate group of the pyrazine ring interact with the lanthanide ions to form a chelate complex.

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To investigate the coordination behaviour of the ring nitrogen in the heterocyclic carboxylate ligands in detail, we are studying the complexation of lanthanide cations with various pyridine-dicarboxylate ligands in aqueous solution. In this paper the thermodynamic parameters of the lanthanide quinolinates are presented. The quinolinate (pyridine-2,3-dicarboxylate) ligand is particularly interesting as the ligand has two possible ways of coordinating to the metal ion. The quinolinate ligand can form a chelate ring by coordinating to the metal ion through either the 1-nitrogen donor-atom and the 2-carboxylate group or through the two carboxylate groups at positions 2 and 3 of the pyridine ring.

EXPERIMENTAL

Chemicals

Stock solutions of the lanthanide perchlorates were prepared by dissolving the lanthanide oxides (Aldrich Co. 99.99%) in hot concentrated perchloric acid and diluting it with deionised water to the appropriate concentration. The stock solutions were standardised by EDTA titration with xylenol orange indicator in acetate buffer. The stock solutions were kept below pH 4 to prevent hydrolysis of the metal ion. Reagent grade quinolinic acid was obtained from Aldrich Co. and used without further purification. The stock solution of quinolinic acid was prepared by dissolving the appropriate weights in standard sodium hydroxide solution and was standardised by acid–base titration. The total ionic strength of the working solutions was adjusted to 0.50 M with $NaClO_4$. Deionised water was used for the preparation of all solutions.

Apparatus

The potentiometric (pH) titrations were performed using a Beckman 4500 digital pH meter in conjunction with a Fisher standard combination electrode. The KCl solution of the electrode was replaced with 4.0 M LiCl solution to prevent the precipitation of $KClO_4$. The pH meter was calibrated using Standard Buffer Solutions (Anachemia Tedia Co.) of pH 7.00 and 4.00. The titrations were conducted at $25.0 \pm 0.1°$C using a jacketed vessel connected to a circulating water bath. The calorimetric titrations were performed on a titration calorimeter which is similar to the commercially available Tronac Model 450 calorimeter.

Procedures

Potentiometric (pH) titrations were used to determine the acid constants of the quinolinic acid and the stability constants of the lanthanide quinolinate complexes. The proton dissociation constant of quinolinic acid was determined by titrating a 20.0 ml aliquot of the ligand acid solution with a standard NaOH solution. The stability constants of the lanthanide quinolinate complexes were determined by titrations of lanthanide perchlorate solutions with the quinolinate buffer solution.

Calorimetric titrations were employed to determine the enthalpies of protonation of the quinolinic acid and the enthalpies of complexation of lanthanide quinolinate complexes. The heats of protonation of the ligand acid were obtained by titrating calorimetrically the quinolinate solution with a standard HCl solution. The heats of formation of the lanthanide quinolinate complexes were determined by subtracting the heats of dilution and protonation of the ligand from the heat obtained by the titration of the lanthanide perchlorate solutions with the ligand buffer solution. The heats of dilution of the ligand were determined by titration of the ligand solution into 0.50 M $NaClO_4$ solution.

In all titrations, the ratio of the concentrations of the metal ion and the ligand was maintained such that ML_2 complexes were not formed. The titration data were treated by linear least-squares analysis.

RESULTS

Typical sets of potentiometric and calorimetric titration data of the Eu(III)-quinolinate system are given in Tables 1 and 2, respectively. In Fig. 1, corrected heats evolved in the titration are plotted against the calculated moles of the complex formed. The experimental results fit well with the calculated data.

The thermodynamic parameters of the step-wise protonation of quinolinate in a medium of 0.50 M ($NaClO_4$) ionic strength at 25.0 °C are

TABLE 1

Potentiometric titration data for Eu(III)–quinolinate system; $\mu = 0.50$ M ($NaClO_4$); $T = 298$ K [a]

Vol. of titrant (ml)	pH	$10^4[L]$ M	$\bar{n}$
0.50	3.926	0.314	0.091
1.00	3.849	0.561	0.163
1.50	3.820	0.813	0.220
2.00	3.806	1.061	0.271
2.50	3.799	1.306	0.319
3.00	3.798	1.557	0.363
3.50	3.799	1.806	0.405
4.00	3.803	2.062	0.443

[a] Initial volume = 20.0 ml; initial pH 4.167; $C_M = 9.92 \times 10^{-4}$ M; $C_L = 1.010 \times 10^{-2}$ M; $C_H = 7.43 \times 10^{-3}$ M.

TABLE 2

Calorimetric titration data for Eu(III)-quinolinate system; $\mu = 0.50$ M ($NaClO_4$); $T = 298$ K [a]

Vol. of titrant (ml)	Q_{corr} (mJ)	$10^4 \times n_{ML}$ (mol)	Vol. of titrant (ml)	Q_{corr} (mJ)	$10^4 \times n_{ML}$ (mol)
0.101	52.5	0.145	1.111	510.0	1.479
0.202	102.9	0.289	1.212	549.6	1.590
0.303	153.4	0.431	1.313	589.6	1.693
0.404	201.8	0.572	1.414	627.7	1.787
0.505	248.3	0.711	1.515	665.9	1.872
0.606	294.9	0.848	1.616	701.9	1.945
0.707	339.5	0.983	1.717	737.6	2.007
0.808	382.2	1.113	1.818	770.2	2.056
0.909	425.2	1.240	1.919	779.1	2.091
1.010	468.5	1.363	2.020	825.8	2.111

[a] Initial volume = 50.0 ml; initial pH 4.436; $C_M = 1.891 \times 10^{-2}$ M; $C_L = 1.481 \times 10^{-1}$ M.

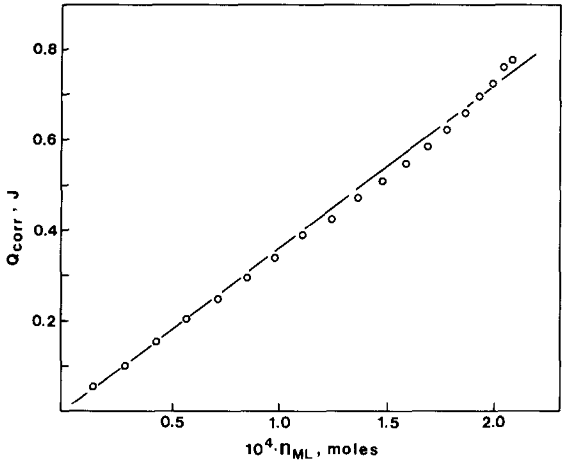

Fig. 1. Plot of the corrected heat versus calculated number of moles of the species, ML, formed during the calorimetric titration.

TABLE 3

Thermodynamic values of step-wise protonation of quinolinate ligands; $\mu = 0.50$ M ($NaClO_4$); $T = 298$ K

Species	$\log K_a$ [a]	$-\Delta G$ (kJ mol^{-1})	ΔH [b] (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
HL	4.52 ± 0.01	25.82 ± 0.07	-1.72 ± 0.01	80.8 ± 0.3
H_2L	6.71 ± 0.02	38.31 ± 0.11	8.34 ± 0.10	156.5 ± 0.6

[a] The HL values are for the reaction $H + L \rightleftharpoons HL$; the H_2L values are for $2H + L \rightleftharpoons H_2L$.
[b] $\Delta H_{ML} = \Delta H_{011}$ and $\Delta H_{H_2L} = \Delta H_{021}$.

TABLE 4

Thermodynamic parameters for lanthanide(III)–quinolinate complexation; $\mu = 0.50$ M ($NaClO_4$); $T = 298$ K

Ion	$\log \beta_{101}$	$-\Delta G_{101}$ (kJ mol^{-1})	ΔH_{101} (kJ mol^{-1})	ΔS_{101} (J K^{-1} mol^{-1})
La	2.96 ± 0.01	16.90 ± 0.01	4.55 ± 0.51	72.0 ± 1.7
Nd	3.49 ± 0.01	19.92 ± 0.02	1.96 ± 0.09	73.4 ± 0.4
Sm	3.67 ± 0.01	20.97 ± 0.05	2.26 ± 0.09	77.9 ± 0.4
Eu	3.60 ± 0.01	20.52 ± 0.05	3.56 ± 0.14	80.8 ± 0.6
Gd	3.53 ± 0.01	20.17 ± 0.02	4.40 ± 0.28	82.4 ± 1.0
Dy	3.78 ± 0.01	21.56 ± 0.08	4.18 ± 0.24	86.3 ± 0.9
Ho	3.78 ± 0.01	21.57 ± 0.03	3.82 ± 0.20	85.2 ± 0.7
Er	3.90 ± 0.01	22.25 ± 0.06	3.36 ± 0.22	85.9 ± 0.8
Yb	4.03 ± 0.01	23.00 ± 0.08	2.45 ± 0.13	85.3 ± 0.6
Lu	4.02 ± 0.02	22.93 ± 0.10	2.08 ± 0.07	83.9 ± 0.5

listed in Table 3. Table 4 summarises the thermodynamic parameters calculated for the formation of the lanthanide quinolinate complexes in 0.50 M $NaClO_4$ medium at 25.0 °C. The error limits indicate one standard deviation. The definition of β_{101}, ΔH_{101} and ΔS_{101} are as given in the literature [10–13].

DISCUSSION

The quinolinate ligand has three donor sites: a nitrogen atom at position 1 and two oxygen atoms of two carboxylate anions at positions 2 and 3 of the pyridine ring. The simultaneous binding of all three donor sites with the metal ion is sterically prohibited. The quinolinate ligand could coordinate to the metal ion to form a five-membered chelate through the nitrogen atom at position 1 and the carboxylate anion at position 2, or a seven-membered chelate through two carboxylate anions at positions 3 and 4 of the pyridine ring. Figure 2 suggests that the quinolinate ligand behaves as the former structure. The variation of the thermodynamic parameters with the atomic number of lanthanide reflects the dehydration and bonding effects in the complexation [12,14–16]. Figure 2 shows the variation of the thermodynamic parameters (ΔG_{101}, ΔH_{101} and $T\Delta S_{101}$) of the lanthanide complexes of α-picolinate and quinolinate across the lanthanide series. The trends of the variations are similar to each other for the complexes of quinolinate and α-picolinate. This means that the quinolinate ligand forms the chelate complex with lanthanide cations in the same way as the α-picolinate. It is known that the nitrogen donor atom at position 1 of the heterocyclic ring and the carboxylate anion at position 2 of the ligand are involved in the chelate formation of the α-picolinate [3–5] and pyrazinecarboxylate systems [7,8].

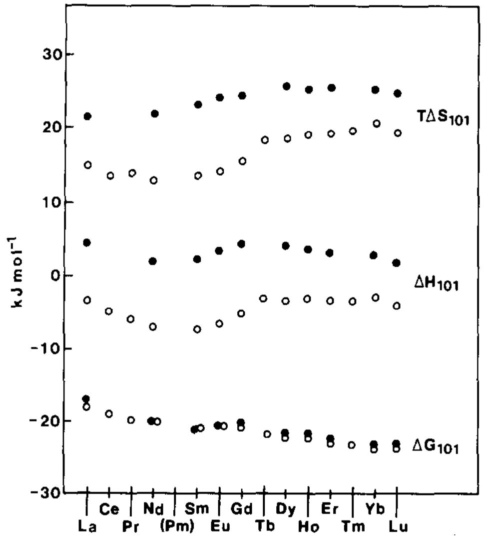

Fig. 2. Variation of thermodynamic parameters (ΔG_{101}, ΔH_{101} and $T\Delta S_{101}$) of complexation of Ln(III) across the lanthanide series; ●, quinolinate; ○, α-picolinate.

Table 5 lists the thermodynamic data for some samarium(III) complexes. It is known that there is a linear relationship between the stability constants (log β_{101}) and the ligand acidity constants (ΣpK_a) for a number of carboxylate complexes of lanthanide in aqueous solution [11–13]. Figure 3 is the plot of log β_{101} against ΣpK_a of the ligand for some Sm(III) complexes. The values of log β_{101} have been adjusted, if necessary, to an ionic strength of 0.1 M in $NaClO_4$ solution according to the method described in the literature [18]. The log β_{101} values for the quinolinate, α-picolinate and pyrazinecarboxylate are above the correlation line, which reflects more stabilisation than expected. They are also more stable than the chelate complexes formed by the alkanedicarboxylate ligands such as the succinate, glutarate and adipate [13]. This also supports the conclusion that the lanthanide quinolinate complexes are five-membered chelates formed by the binding of lanthanide ion to the ligand through the 1-nitrogen atom and 2-carboxylate group of the pyridine ring.

Figure 4 is a plot of the correlation of the enthalpy of complexation, ΔH_{101}, and the entropy of complexation, ΔS_{101}, for some Sm(III) complexes. It shows a linear relationship with an isothermodynamic temperature of 177 K for the monocarboxylate monodentate and dicarboxylate monodentate ligands. However, the ligands which have the nitrogen donor atom at position 1 of the ring, such as the α-picolinate, pyrazinecarboxylate and quinolinate, deviate from the relationship and seem to form another linear correlation, together with the anthranilate, with an isothermodynamic temperature of 244 K. Because the temperature studied is 298 K, the entropy effect is the driving force for the complexation for both systems. However,

TABLE 5

Thermodynamic data for some samarium(III)–L complexes; $T = 298$ K [a]

No.	Ligand	Ionic strength (M)	pK_{a1}	pK_{a2}	$\log \beta_{101}$	$-\Delta G_{101}$ (kJ mol^{-1})	ΔH_{101} (kJ mol^{-1})	ΔS_{101} (J K^{-1} mol^{-1})	Ref.
1	Acetate	2.0	4.80		2.03	11.6	6.1	59	10
		0.1	4.56		2.17		(5.6)	(65)	
2	Chloroacetate	0.1	2.86		1.32	7.5			10
3	Iodoacetate	0.1	2.98		1.43	8.2			10
4	Benzoate	0.1	3.99		2.21	12.6	7.6	68	11
5	3-Nitrobenzoate	0.1	3.28		1.85	10.5	5.7	54	12
6	3-Fluorobenzoate	0.1	3.68		1.95	11.1	6.1	58	12
7	4-Fluorobenzoate	0.1	3.95		2.12	12.1	8.0	67	12
8	Isophthalate	0.1	3.30	4.38	2.82	16.1	10.7	90	11
9	Fumarate	0.1	2.85	4.10	2.83	16.1	14.5	103	10
10	*o*-Phthalate	0.1	2.75	4.93	3.70				10
11	Maleate	0.1	1.77	5.85	3.82	21.8	12.7	115	10
12	Anthranilate	0.1	1.97	4.79	4.23	24.1	4.1	95	17
13	Pyrazine-carboxylate	1.0	2.76		2.85	16.3	−0.3	54	7,8
		(0.1)			(3.62)	(20.7)	(−1.3)	(65)	
14	α-Picolinate	0.5	0.86	5.17	3.65	20.8	−7.3	45	4,5
		(0.1)			(4.28)	(24.4)	(−8.3)	(54)	
15	Quinolinate	0.5	2.19	4.52	3.67	21.0	2.3	78	this work
		(0.1)			(4.57)	(26.1)	(1.3)	(92)	

[a] The values in parentheses are estimated values at $\mu = 0.1$ M $NaClO_4$.

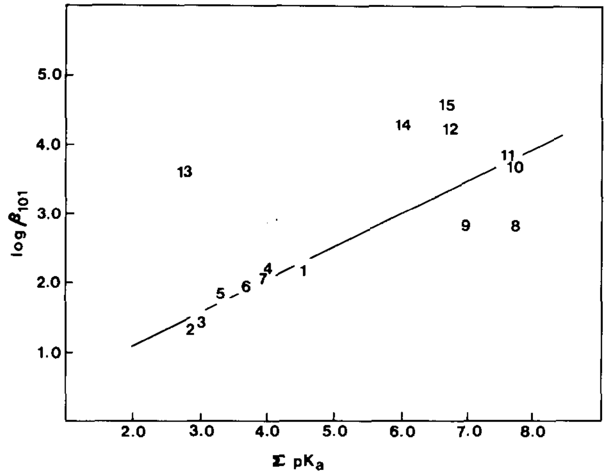

Fig. 3. Relationship between the stability constant, log β_{101}, for formation of Sm(III)–L and the acid constant, ΣpK_a, of H_nL. The ligand corresponding to the numbers are given in Table 5.

the exothermicity of the interaction between the lanthanide cation and the nitrogen donor atom of the ligand also contributes to the stabilisation of the complex of the latter system and would account for the small or negative enthalpies of complexation of the α-picolinate, pyrazinecarboxylate and quinolinate, compared to the alkanecarboxylate systems.

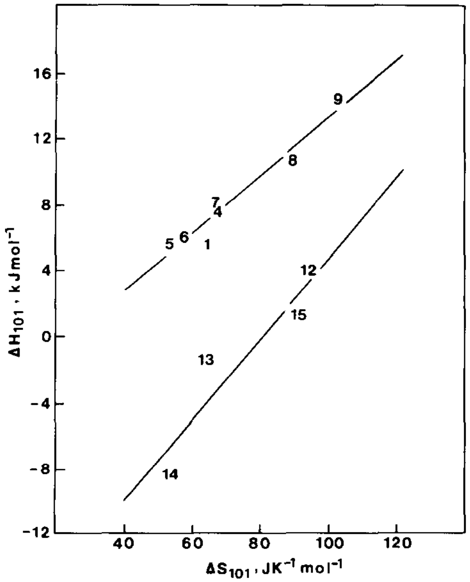

Fig. 4. Relationship between ΔH_{101} and ΔS_{101} for Sm(III)–L complexes.

The enthalphies of complexation for the lanthanide quinolinates are more positive than those for the α-picolinates. For example, the difference in ΔH_{101} between the α-picolinate and quinolinate is 9.6 kJ mol^{-1} for Sm(III) complexes. This enthalpy difference may be due to the additional energy required for the complexation of the quinolinate. In the case of the quinolinate system, the intra-hydrogen bond between the carboxylate groups at positions 2 and 3 would be broken when the metal ion forms a chelate complex by coordinating to the nitrogen donor atom at position 1 and the carboxylate group at position 2 of the pyridine ring. Therefore, extra energy to break the intra-hydrogen bond would be required in the complexation of the quinolinate. The more positive enthalpy of the complexation could be compensated by the entropy gain resulting from the breaking of the intra-hydrogen bond. As expected, the value of ΔS_{101} for the samarium quinolinate is 33 J K^{-1} mol^{-1} more positive than that for the α-picolinate.

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